

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT) -

(51) International Patent Classification ⁷ : C09D 201/02, G03F 7/027, C09D 4/00	A1	(11) International Publication Number: WO 00/55272 (43) International Publication Date: 21 September 2000 (21.09.00)
(21) International Application Number: PCT/EP00/02281 (22) International Filing Date: 14 March 2000 (14.03.00) (30) Priority Data: 99200807.8 16 March 1999 (16.03.99) EP (71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): KJELLQVIST LIN-DELL, Ann, Kerstin, Birgitta [SE/SE]; Linneg 131, S-216 18 Malmö (SE). KRUIHOF, Klaas, Jan, Hendrik [NL/NL]; Debussysstraat 3, NL-3906 BK Veenendaal (NL). LANSBERGEN, Adrianus, Jozefus, Hendricus [NL/NL]; Hogeweg 5, NL-6862 WV Oosterbeek (NL). KLAASEN, Robert, Paul [NL/NL]; Iseoplantsoen 26, NL-1060 PW Amsterdam (NL). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Department (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: RADIATION CURABLE COATING COMPOSITION COMPRISING A SECONDARY CURING AGENT (57) Abstract The invention relates to a radiation curable coating composition, which is formed by mixing (A) a radiation curable lacquer comprising a compound having an olefinically unsaturated double bond with (B) a compound comprising an electron donor-functional group capable of reacting with the compound, which is present in lacquer (A) having an olefinically unsaturated double bond, in the absence of electromagnetic radiation having a wavelength $\lambda \leq 500$ nm. Compound (B) further can comprise a radiation curable-functional group. The invention also relates to a process for coating substrates using the radiation curable coating composition.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

RADIATION CURABLE COATING COMPOSITION COMPRISING A SECONDARY CURING
AGENT

The present invention relates to a radiation curable coating composition
5 comprising a secondary curing agent.

Such a composition is known, e.g., from US 4,128,600, wherein a radiation
curable coating composition is disclosed which comprises a saturated polyol
and a reactive oligomer selected from the group consisting of fully substituted
10 poly(meth)acrylates of poly-functional alcohols. This known composition
additionally comprises a polyisocyanate.

A primary concern in the coating industry is the need to reduce the emission of
volatile hydrocarbons into the air.

15 In classic heat curing coating compositions a high-viscous film forming resin is
mixed with a solvent to aid the manufacture of the coating composition and to
facilitate the application of these compositions to substrates. During curing of
the coating the solvent is driven off by the thermal energy used to effect the
curing. A considerable amount of thermal energy is thus used to drive off the
20 solvent. However, the thermal energy may cause considerable side effects in
the coating or on the substrate, in particular when the substrate is heat
sensitive.

To solve this problem, it was suggested to use a radiation sensitive reactive
solvent to reduce the viscosity of the film forming resin. Upon radiation, these
25 reactive solvents react with each other or with the film forming resin and a
coating of good quality can be obtained. Optionally, the composition may
comprise a crosslinker which reacts with the film forming resin.

A problem with these coatings on porous substrates is the penetration of the
30 coating composition into the pores, in particular when radiation is used to cure

the coating. Since the radiation does not reach these areas, uncured coating material is the result. This can give health, safety, and environmental problems, e.g., when the substrate is cut or sanded. These problems occur even years after the lacquer has been applied. The same problems can be found in other
5 substrates comprising shadow areas, e.g. in 3-D substrates, or when a pigmented lacquer is used.

In particular low-molecular weight material, viz. monomers and oligomers which are used as reactive oligomers, gives the biggest problem with penetration.
10 Well-known acrylic diluents, e.g., tripropylene glycol diacrylate (TPGDA), hexanediol diacrylate (HDDA), and hydroxyethyl methacrylate (HEMA) are irritant and sensitising and will never react if they are not reached by the UV light.

15 To overcome the problems caused by the not yet reacted diluent, it is known in the art to add a secondary curing agent. In general, a secondary curing agent will have a lower reactivity towards the main film forming component(s) than the primary curing agent.

A well-known side effect of the addition of a secondary curing agent to a
20 radiation curable composition is a reduction of the pot life of the thus obtained coating composition, since the secondary curing agent will also react in the absence of radiation.

(Poly)isocyanates are often used as a secondary curing agent if the lacquer is formulated in such a way that only OH-functional acrylic reactive oligomers are
25 used, for instance HEMA. However, the use of isocyanates is not attractive and it limits the formulation possibilities of the lacquer.

Peroxy curing is not preferred, mainly due to handling problems such as short pot life.

In the market nowadays lacquer compositions comprising a carboxy compound
30 and an epoxy secondary curing agent can be found. A major drawback of this

coating formulation is the required balance between reactivity and coating performance. With these systems a fair coating performance can only be obtained after long reaction times. If accelerators for the reaction are incorporated into the formulation, a poor coating performance is observed.

- 5 Moisture curing silanes can also be used as secondary curing agents but require controlled amounts of water to cure. In practice such a controlled environment is often hard to maintain.

DE 33 06 093 discloses a radiation curable binder emulsion prepared by
10 reacting a secondary amine with part of the ethylenically unsaturated double bonds of a polymeric material. In this reaction, the secondary amine is not a secondary curing agent. Further, the mixing of a radiation curable lacquer having unsaturated double bonds with a compound comprising an electron donor-functional group is not mentioned.

- 15 EP 0 447 945 discloses the preparation of an amine modified urethane acrylate binder. In this reaction, the amine compound is reacted with an unsaturated double bond in the urethane acrylate binder. This reaction is one of the steps in the preparation of a radiation curable coating composition. In this reaction, the secondary amine is not a secondary curing agent. Further, the mixing of a
20 radiation curable lacquer having unsaturated double bonds with a compound comprising an electron donor-functional group is not mentioned.

The present invention relates to a radiation curable coating composition which presents a solution to the above-mentioned problems, viz. a radiation curable
25 coating composition which is obtained by mixing (A) a radiation curable lacquer comprising a compound having an olefinically unsaturated double bond with (B) a compound comprising an electron donor-functional group capable of reacting with the compound, which is present in lacquer (A) having an olefinically unsaturated double bond, in the absence of electromagnetic radiation having a
30 wavelength $\lambda \leq 500$ nm.

It was found that a broad range of radiation curable lacquers comprising unsaturated polymer resins, optionally including reactive oligomers, and compounds comprising an electron donor-functional group can be used in the composition according to the present invention.

The amount of compound B (i.e. the compound comprising an electron donor-functional group) that is mixed with the radiation curable lacquer should be such that a balance is found between the reactivity of the electron donor-functional group towards the radiation curable lacquer and the stability of the coating composition. In general, good results are obtained when 1 - 20 pbw of compound B are mixed with 100 pbw of the radiation curable lacquer composition A.

Within the framework of the present invention, a radiation curable coating composition is a coating composition which is cured by using electromagnetic radiation having a wavelength $\lambda \leq 500$ nm. Examples of electromagnetic radiation having a wavelength $\lambda \leq 500$ nm are, e.g., UV radiation or electron beam radiation.

Within the framework of the present invention the radiation curable lacquer (A) is a coating composition that is capable of curing and film forming without the necessity to add any further components and that will provide a coating with good properties, albeit that the cured coating then may comprise unreacted monomers and/or oligomers.

Preference is given to the use of a lacquer comprising UV curing unsaturated polymer resins, such as UV curable unsaturated polyester resins, UV curable unsaturated epoxy resins, UV curable unsaturated urethane resins, and UV curable unsaturated acrylic resins or mixtures thereof.

Examples of unsaturated polymer resins that can be used in the coating composition according to the present invention are Laromer® 8799 (ex BASF) Craynor® 104 (ex Cray Valley), Ebercyl® 210 (ex UCB), Crodamer® UVE 150 (ex Croda) or Actilane® 578 (ex Akcros).

5

To obtain a suitable application viscosity of the coatings, well-known UV curable monomers can be added as viscosity reducing agents and reactive oligomers. Examples of these reactive oligomers are tripropylene glycol diacrylate (TPGDA), hexanediol diacrylate (HDDA), and hydroxyethyl methacrylate (HEMA).

10

Good results are obtained when the compound comprising an electron donor-functional group is an amine- or thio-functional compound.

If an amine compound is used as compound comprising an electron donor-functional group, special attention should be paid to the reactivity of the amine compound towards the radiation curable lacquer. In general, primary amine compounds show a high reactivity towards unsaturated double bonds, leading to a relatively short pot life. The reactivity can be decreased by sterically hindering, shielding or capping the primary amine group.

15

In general, good results are obtained when the amine-functional compound is a secondary amine compound. These compounds show a very good balance between reactivity and stability. Examples of amine-functional compounds which give very good results in the coating composition according to the present invention are aminoethyl ethanolamine, aminoethyl piperazine, α,ω -diaminopropylene glycol (Jeffamine D400), diethylene triamine, dipropylene triamine, trimethylhexane(1,6)diamine (mixture of 2,2,4 and 2,4,4 isomers), and 3-aminopropyltriethoxysilane (Dynasil AMEO-T ex Hüls).

20

25

Examples of thio-functional compounds that can be used in the coating composition according to the present invention are the esters of thioglycolic

30

acid, 1-mercaptopropionic acid or 2-mercaptopropionic acid with polyols, such as glycols, pentaerythritol, di-pentaerythritol, and trimethylol propane. Specific examples of suitable thiols are ethylene glycol bis (thioglycolate), ethylene glycol bis (2-mercaptopropionate), pentaerythritol tetrakis (thioglycolate), and
5 pentaerythritol tetrakis (3-mercaptopropionate).

Due to the presence of a compound comprising an electron donor-functional group capable of reacting in the absence of radiation with the compound having an olefinically unsaturated double bond in the coating composition according to
10 the present invention, a secondary curing mechanism occurs which reduces the amount of uncured reactive species. This can be shown by several well-known analytical techniques, e.g., by extraction analysis.

If the electron donor-functional group is an amine- or thio-functional group, the compound comprising such groups undergoes a Pseudo Michael Addition
15 (PMA) to the unreacted $c=c$ bonds which are present in the lacquer composition. The double bonds not cured by the UV light will then be cured by PMA. In principle, there is no limitation of the formulation possibilities.

In general, the reaction between the electron donor-functional group and the
20 unsaturated double bond will start when components (A) and (B) are mixed.

When the electron donor-functional group is an amine- or thio-functional group, in particular when the amine-functional group is a secondary amine group, a very good balance is obtained between the stability of the coating formulation and its reactivity. Without any special precautions, with these compositions a
25 pot life between 6 and 8 hours can be obtained.

To further improve the film properties of the coating composition according to the present invention, a radiation curable group can be incorporated into the compound comprising an electron donor-functional group. Particularly good
30 results can be obtained if the radiation curable group is incorporated by

reacting a so-called bulky unsaturated monomer with the compound comprising the electron donor-functional group. For example, by reacting DCPA (dicyclopentenyl acrylate, i.e. a bulky unsaturated monomer) with DETA (diethylenetriamine) or DPTA (dipropylenetriamine) an amine-functional
5 electron donor compound is obtained with two UV curable groups, viz. the two dicyclopentenyl groups. This so-called dual-cure amine-functional compound can react with the unreacted c=c bonds which are present in the coating composition and can play a role in the curing of the coating when the coating is irradiated by actinic rays.

10

It was found that the radiation reactivity of the coating compositions according to the present invention is improved in comparison to known radiation curable coating compositions.

Further, with the composition according to the present invention, an improved
15 through-cure and adhesion to the substrate was found in comparison to similar known coating compositions.

In addition, it was found that also the abrasion resistance of the coating compositions according to the present invention is improved in comparison to known radiation curable coating compositions, for example radiation curable
20 lacquers comprising a compound having an olefinically unsaturated double bond but which do not contain a compound comprising an electron donor-functional group capable of reacting with the compound, which is present in lacquer (A) having an olefinically unsaturated double bond.

25 The coating compositions according to the present invention are particularly suited to be used as a radiation curable coating for substrates comprising shadow areas, such as 3D substrates or porous substrates like paper, wood or MDF, but they can also be used for the coating of metal or plastic substrates. Further, the coating compositions according to the present invention are very

well suited to be used in (heavily) pigmented radiation curable coating compositions.

Additives and fillers that are known to those skilled in the art can be added to
5 the coating compositions according to the present invention, e.g., diluents, defoamers, levelling agents, antissettling agents, photoinitiators, rheology modifiers, and pigments.

The invention will be elucidated with reference to the following examples. These
10 are intended to illustrate the invention but are not to be construed as limiting in any manner the scope thereof.

Examples

15 Example 1

An abrasion resistant UV curable basecoat is prepared by combining 61 parts by weight of an polyester acrylate binder, 30 parts by weight of an acrylic diluent (25,3 parts by weight of which are tripropylene glycol diacrylate [TPGDA]), and 9 parts by weight of other components such as photoinitiators,
20 defoamers, levelling agents, and fillers.

Example 2

A UV curable basecoat for furniture is prepared by combining 34,6 parts by weight of a polyester acrylate binder, 44,8 parts by weight of a polyether
25 acrylate binder, and 17 parts by weight of other components such as photoinitiators, defoamers, levelling agents, and fillers.

Example 3

Several amine-functional resins are prepared on the basis of an acrylate and a
30 secondary amine. Optionally TPGDA is added. The resins are prepared by

slowly adding the acrylate (DCPA: dicyclopentenylacrylate) to the amine. When TPGDA is added, it is added before the acrylate. The obtained mixture is cooled with ice/water in order to keep the temperature below 15°C. Approximately one hour after the addition, the reaction is completed. This can
 5 be checked by Proton NMR on acrylic protons, which should no longer be present. The following amine-functional resins were prepared:

Resin no.	Type of amine	Molar ratio amine/DCPA/TPGDA
3a	AEEA	1:1
3b	AEEA	1:1,25
3c	AEEA	1:1,5
3d	AEP	1:1
3e	DETA	4:5:1,5
3f	DPTA	4:5:1,5
3g	TMHDA	4:5:1,5

Wherein

- 10 AEEA stands for aminoethyl ethanolamine
 AEP stands for aminoethyl piperazine
 DETA stands for diethylene triamine
 DPTA stands for dipropylene triamine
 15 TMHDA stands for trimethylhexane(1,6)diamine (mixture of 2,2,4 and 2,4,4 isomers)

For comparison, a solution was prepared of 70 wt.% Desmodur N (a polyisocyanate) in 30 wt.% ethylacetate. In the following, this resin is indicated as resin 3h.

20

Example 4

The curing time of some lacquer compositions was measured using a transport belt and a 80 W/cm² Hg lamp. The lacquer was applied to a substrate that was placed on the belt. The substrate was passed under the Hg lamp. The speed of

the belt was adjusted to get a fully cured lacquer after one passage under the lamp. The higher the belt speed, the shorter the curing time of the lacquer.

In this way the effect of the addition of some resins of Example 3 on the reactivity of the lacquer of Example 1 was measured.

5

Lacquer composition	Belt speed (m/min)
Example 1	7
Example 1 + 6,45 wt.% of resin 3a	> 25
Example 1 + 6,45 wt.% of resin 3b	23
Example 1 + 6,45 wt.% of resin 3c	20
Example 1 + 6,45 wt.% of resin 3d	23
Example 1 + 6,45 wt.% of resin 3e	19
Example 1 + 6,45 wt.% of resin 3f	22
Example 1 + 6,45 wt.% of resin 3g	13
Example 1 + 6,45 wt.% of resin 3h	8

Example 5

Some resins of Example 3 are added to the lacquer of Example 1. The resulting
10 lacquer is applied with a roller on oak parquet panels at 25-30 g/cm² and precured using Hg lamps with 80 W/cm² on a belt at a speed of 10 m/min. A second lacquer layer is applied at 25-30 g/cm² and cured at 5 m/min.

The amount of acrylic diluent in the obtained lacquer layer is determined by peeling 1 dm² with a depth of 2-3 mm off the panels and extraction with
15 dichloromethane followed by gaschromatographic measurements (GC/FID). In this way the total amount of acrylic diluents in the lacquer is measured.

The following results are found:

Lacquer composition	Acrylic diluents mg/dm ²
Example 1	14
Example 1 + 6,45 wt.% of resin 3a	9,5
Example 1 + 6,45 wt.% of resin 3b	7
Example 1 + 6,45 wt.% of resin 3c	7
Example 1 + 6,45 wt.% of resin 3d	7
Example 1 + 10,0 wt.% of resin 3e	10
Example 1 + 10,0 wt.% of resin 3f	7
Example 1 + 10,0 wt.% of resin 3g	10
Example 1 + 9,2 wt.% of resin 3h	12,5

Example 6

- 5 Example 5 is repeated using the lacquer of Example 2. This lacquer is applied on MDF substrates.

The following results are found:

Lacquer composition	Acrylic diluents mg/dm ²
Example 2	5,5
Example 2 + 10,0 wt.% of resin 3a	2,9
Example 2 + 10,0 wt.% of resin 3b	1,1
Example 2 + 10,0 wt.% of resin 3e	2,6
Example 2 + 10,0 wt.% of resin 3f	2,7
Example 2 + 10,0 wt.% of resin 3h	4,2

Example 7

The abrasion resistance of panels prepared according to Example 5 is measured using the falling sand method SIS 923509.

The following results are found:

5

Lacquer composition	Abrasion mg/100 rev.
Example 1	5,2
Example 1 + 10,0 wt.% of resin 3a	1,5
Example 1 + 10,0 wt.% of resin 3d	1,5
Example 1 + 10,0 wt.% of resin 3e	1,7
Example 1 + 10,0 wt.% of resin 3g	1,7
Example 1 + 9,2 wt.% of resin 3h	2,6

Claims

1. Radiation curable coating composition which is formed by mixing (A) a radiation curable lacquer comprising a compound having an olefinically unsaturated double bond with (B) a compound comprising an electron donor-functional group capable of reacting with the compound, which is present in lacquer (A) having an olefinically unsaturated double bond, in the absence of electromagnetic radiation having a wavelength $\lambda \leq 500$ nm.
2. Radiation curable coating composition according to claim 1, characterised in that the compound comprising the electron donor-functional group is an amine- or thio-functional compound.
3. Radiation curable coating composition according to claim 1, characterised in that the amine-functional compound is a secondary amine compound.
4. Radiation curable coating composition according to claims 1-3, characterised in that compound (B) also incorporates a radiation curable-functional group.
5. Process for coating a substrate with a radiation curable coating composition wherein prior to application to the substrate the composition is formed by mixing (A) a radiation curable lacquer comprising a compound having an olefinically unsaturated double bond with (B) a compound comprising an electron donor-functional group capable of reacting with the compound, which is present in lacquer (A) having an olefinically unsaturated double bond, in the absence of electromagnetic radiation having a wavelength $\lambda \leq 500$ nm.

6. Process according to claim 5, characterised in that the compound comprising the electron donor-functional group is an amine- or thio-functional compound.
- 5 7. Process according to claim 5, characterised in that the amine-functional compound is a secondary amine compound.
8. Process according to any one of claims 5 - 7, characterised in that compound (B) also incorporates a radiation curable-functional group.
- 10 9. Process according to any one of claims 5-8, characterised in that the substrate is a substrate comprising shadow areas.
- 15 10. Use of the coating composition according to any one of claims 1 to 4 for the coating of substrates comprising shadow areas.

INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/EP 00/02281

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D201/02 G03F7/027 C09D4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 33 06 093 A (VIANOVA KUNSTHARZ) 3 November 1983 (1983-11-03) page 12, line 1 - line 10 page 10, line 10 - line 30	1-8
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 28 (C-471), 27 January 1988 (1988-01-27) & JP 62 179519 A (MATSUSHITA ELECTRIC IND CO LTD), 6 August 1987 (1987-08-06) abstract & DATABASE WPI Week 8737 Derwent Publications Ltd., London, GB; AN 260120	1-8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 June 2000

Date of mailing of the international search report

30/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Lensen, H

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/02281

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 447 845 A (BASF AKTIENGESELLSCHAFT) 25 September 1991 (1991-09-25) page 3, line 20 - line 40 page 5, line 6 - line 15 ----	1-4
Y	PATENT ABSTRACTS OF JAPAN vol. 14, no. 356 (C-745), 2 August 1990 (1990-08-02) & JP 02 129213 A (WASHIN KAGAKU KOGYO KK), 17 May 1990 (1990-05-17) abstract & DATABASE WPI Week 9026 Derwent Publications Ltd., London, GB; AN 196898 ----	1-4
A	US 5 460 857 A (STEPHAN SCHUNCK) 24 October 1995 (1995-10-24) ----	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 316 (C-524), 26 August 1988 (1988-08-26) & JP 63 085030 A (MITSUBISHI PETROCHEM) abstract & DATABASE WPI Week 8821 Derwent Publications Ltd., London, GB; AN 143632 abstract ----	
X	PATENT ABSTRACTS OF JAPAN vol. 16, no. 137 (M-1231), 7 April 1992 (1992-04-07) & JP 03 297638 A (HITACHI CHEM), 27 December 1991 (1991-12-27) abstract & DATABASE WPI Week 199230 Derwent Publications Ltd., London, GB; AN 59282 abstract -----	1,2,5,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/02281

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3306093 A	03-11-1983	AT 376230 B AT 120182 A	25-10-1984 15-03-1984
JP 62179519 A	06-08-1987	JP 1949233 C JP 6078409 B	10-07-1995 05-10-1994
EP 447845 A	25-09-1991	DE 4007146 A AT 122039 T DE 59105353 D DK 447845 T ES 2071141 T JP 4220420 A US 5442090 A	12-09-1991 15-05-1995 08-06-1995 17-07-1995 16-06-1995 11-08-1992 15-08-1995
JP 02129213 A	17-05-1990	NONE	
US 5460857 A	24-10-1995	DE 4118731 A AT 118379 T BR 9206107 A CZ 9302667 A DE 59201420 D DK 587591 T WO 9221450 A EP 0587591 A ES 2071503 T HU 67387 A PL 168037 B SK 137693 A	10-12-1992 15-03-1995 10-10-1995 13-04-1994 23-03-1995 17-07-1995 10-12-1992 23-03-1994 16-06-1995 28-04-1995 30-12-1995 11-05-1994
JP 63085030 A	15-04-1988	NONE	
JP 03297638 A	27-12-1991	JP 2041479 C JP 7073898 B	09-04-1996 09-08-1995